PARAMAGNETISM OF SINGLE CRYSTALS OF THE SALTS OF THE IRON GROUP OF ELEMENTS AT LOW TEMPERATURES, PART III, SIX CO-ORDINATED IONIC SALTS OF Cu^{++} AND Fe^{++} IONS

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(*Received for publication, Aug. 28, 1948*)

ABSTRACT. In the present part of the paper the *reciprocally related* D-state ions Cu^{++} and Fe^{++} are discussed. The Stark-pattern of such states, under a predominantly cubic crystalline field with a feeble rhombic component, consists of a doublet and a triplet. For 6-co-ordinated Cu^{++} salts the doublet lies lowest, whereas the pattern ie inverted for similar iron salts. But experimentally, the result of this inversion from Cu^{++} to Fe^{++} is not obvious, since, both show large anisotropies and deviations of the effective moments from the *spin only* value. An explanation is attempted to be given of the observed behaviour of Cu^{++} and Fe^{++} salts namely, that in the former the orbital contribution is confined to a single direction in the crystal and in the latter these act *against* the spin in some of the directions and *for* the spin in others. For the Cu^{++} salts from known X-ray data for the crystals a correlation is given between the *ionic* and the *crystalline* moments. The variation with temperature of the angle between the different ionic groups is calculated and an explanation for the change in the orientation of the magnetic axes of the crystal is given on this basis. From these studies, it is plausible to ascribe not only the cubic but also the small rhombic part of the field to the charged particles in the immediate neighbourhood of the paramagnetic ion. Further, it is reasonable to conclude that the disposition of charged atoms about the paramagnetic ion and hence the crystalline field symmetry for a particular ion, is largely decided by the degeneracy of the ion itself. The temperature variation of the moments of the Fe^{++} ion have an apparent similarity to the Co^{++} ions but unlike cobalt all the principal moments tend to *spin only* value at high temperatures showing the relative unimportance of high frequency contributions in Fe^{++}.

INTRODUCTION

In the two earlier parts of the present paper (Bose, 1948), it has been made sufficiently clear how the crystalline electric field theory of Van Vleck (1932), Penney and Schlapp (1932), Görter (1932) and others, has successfully explained the behaviour of the F-state ions Ni^{++} and Co^{++}. It was shown that under a predominant cubic field with a small rhombic field superimposed upon it the ground state of an F-state ion is split up into a singlet and two adjacent triplets. For the Ni^{++} ion the lowest lying level in this Stark-pattern is the singlet when the cubic field potential is positive, whereas, for the same type of field the triplet lies lowest for Co^{++} ion. On the other hand, the situation is exactly reversed with a negative value of the potential. Such an

TABLE I

For Principal Anisotropies of Crystals

$CuSO_4(NH_4)_2SO_4, 6H_2O$ Monoclinic; $\beta = 106°6'$ $a:b:c = 0.7433:1:0.4838$				$CuSO_4K_2SO_4, 6H_2O$ Monoclinic; $\beta = 104°30'$ $a:b:c = 0.7490:1:0.5088$				$CuSo_4, 5H_2O$ Triclinic; $\alpha:\beta:\gamma = 82°6'$. $107°26'. : 102°40'$. $a:b:c = 0.5721:1:0.5554$		$FeSO_4(NH_4)_2SO_4, 6H_2O$ Monoclinic, $\beta = 106°48'$. $a:b:c = 0.7466:1:0.4950$				$FeSO_4K_2SO_4, 6H_2O$ Monoclinic; $\beta = 104°32'$ $a:b:c = 0.7377:1:0.5020$		
(1) 'b' axis vertical. (2) 'a' axis vertical, 'b' axis along field				(1) 'b' axis vertical. (2) 'a' axis vertical, 'b' axis along field.				Anisotropy values are taken from measurements by Krishnan and Mukherji (1936-38)		(1) 'b' axis vertical. (2) $(20\bar{1})$ plane vertical and 'b' axis horizontal and along the field*				(1) 'b' axis vertical (2) 'a' axis vertical, 'b' axis along the field			
Temp. °K.	Angle** between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp. °K	Angle** between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp. °K	$\chi_1(=\chi_3) - \chi_2$ $\times 10^6$	Temp. °K	Angle* between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp. °K	Angle** between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$
303.1	−61	300.0	63.5	303.1	−88.0	367.0	74.5	303.1	275 0	303.1	− 37	2582	224	303.1	−43 8	1841	− 345.2
280	−64.7	337 7	117.1	280	−89.4	393.8	81.2	280	290 0	280	− 37	3091	263	280	−43 8	2125	− 426.0
260	−67-0	374 4	161.7	260	−90.3	422 5	88 8	260	306.5	260	− 37	3637	313	260	−43 8	2428	− 515 0
240	−68.3	412.1	200.3	240	−91.2	455.0	97.0	240	327.0	240	− 36.5	4315	372	240	−43 8	2788	− 628.0
220	−69.1	455.4	238.7	220	−92.0	494.9	108.8	220	352.1	220	− 36	5177	443	220	−43 8	3218	− 774 0
200	−69.8	504.4	239.6	200	−92.6	544.3	125.6	200	383 9	200	− 36	6267	535	200	−44 8	3747	− 938.0
180	−70.3	560.3	322.8	180	−93.1	602.7	142 6	180	423.8	180	− 36	7698	658	180	−44 8	4422	−1164
160	−70.8	629.0	373.6	160	−93.5	671.9	160.8	160	471.8	160	− 36	9649	822	160	−44.8	5311	−1489
140	−71.1	712.0	431 6	140	−93.8	759 8	181.4	140	535.4	140	− 35	12330	1039	140	−44.8	6572	−2015
120	−71.1	824.1	502.0	120	−94.0	878 4	206.7	120	615.5	120	− 35	16540	1365	120	−45 8	8612	−2566
100	−71.1	1013	629.9	100	−94.0	1052	248.1	100	717.8	100	− 35	22840	1900	100	−45 8	11510	−3162
92.9	−71.1	1109	698.0	90	−94.0	1155	276 4	90	782.0	90	− 35	26,20	2270	90	−45 8	13550	−3467
—	—	—	—	83.9	−94.0	1226	298 2	88 7	789.5	84.8	− 35	29090	2465	86.3	−45 8	14440	−3558

* Angle (001) : $(20\bar{1}) = 64°5'$ ** Angle measured in degrees.

inversion of Stark-pattern should generally occur, as was mentioned in the earlier papers, for the "reciprocally related" ions *i. e.*, for those ions in which the incomplete $3d$ shell contains n or $5+n$, and $5-n$ or $10+n$ electrons respectively. The remarkable differences in the magnetic behaviours of such ions are beautifully demonstrated by the six-coordinated salts of Ni^{++} and Co^{++} and also the four-coordinated blue cobalt salts. Thus we should expect similar widely divergent properties in the Cu^{++} and Fe^{++} salts also, in which the numbers of electrons in the $3d$ shells are nine and six, respectively.

With the same experimental techniques as before we studied the monoclinic ammonium and the potassium Tutton salts of Cu^{++} and Fe^{++} and also the triclinic salt $CuSO_4$, $5H_2O$. The principal magnetic anisotropies $\chi_1-\chi_2$ and $\chi_1-\chi_3$ are given in Table I and the squares of the principal magnetic moments and the mean moments in terms of the Bohr magneton in Table II. Figures 1 – 5 indicate graphically the variations of these quantities with absolute temperature.

TABLE II

For the Gm. Molecular Principal Susceptibilities and the Squares of the Effective Magnetic Moments. (*Corrected for Diamagnetism*)

Crystal	Crystal suspension & the direction along which the susceptibility is measured, *i.e.*, the direction setting along field	Temp. °K	$\chi_1 \times 10^6$	$\chi_2 \times 10^6$	$\chi_3 \times 10^6$	p^2_1	p^2_2	p^2_3	p^2
$CuSO_4$, $5H_2O$	'c' axis vertical, (100) plane at 27°.2 and 110) at 53° 3 to the field χ measured = χ_1 approx	295.2	1650	1370	$\chi_1=\chi_3$	3.923	3.258	$p^2_1=p^2_3$	3.701
		230.0	2116	1768		3.920	3.277		3 706
		168 8	2871	2422		3.904	3.294		3.701
		88.7	5337	4549		3.814	3.251		3.626
$CuSO_4(NH_4)_2$ SO_4, $6H_2O$.	(001) plane vertical, 'b' axis horizontal and along field	295.9	1709	1397	1628	4.072	3.330	3.881	3.761
		225.0	2289	1850	2063	4.149	3 354	3 740	3.748
		173 6	2910	2328	2571	4.069	3 256	3 59	3 640
		124.9	4124	3333	3642	4 150	3 354	3 604	3 723
		92 9	5554	4445	4856	4 157	3.327	3.634	3.706
$CuSO_4K_2SO_4$ $6H_2O$	'b' axis vertical, χ_1 axis along the field	295 9	1696	1321	1619	4.013	3.149	3.859	3.683
		176.9	2800	2188	2655	3.990	3.117	3 783	3.630
		83 9	5824	4597	5525	3 935	3.107	3.734	3.592
$FeSO_4(NH_4)_2$ SO_4, $6H_2O$	(201) plane vertical, 'b' axis horizontal & along field	296.8	13893	10189	12062	30.83	24.36	30.28	28.49
		182.5	22162	14670	21522	32 58	22.57	31 63	28.59
		84 8	50227	21137	17762	34.32	14 44	32.62	27.13
$FeSO_4K_2$ SO_4, $6H_2O$	'a' axis vertical, 'b' axis along field	296 8	12463	10553	12825	29.80	25.23	30 67	28.57
		185.6	19577	15370	20665	29.27	22.98	30 90	27 72
		86.3	41277	26837	44835	28 69	18.65	31 18	26.17

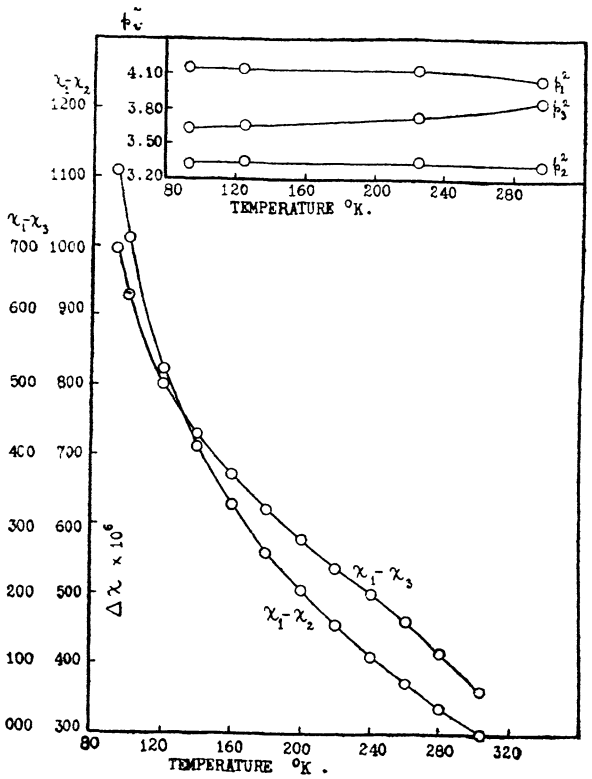


FIG. 2

Temperature Variation of Principal Anisotropies and Effective Moments of $CuSO_4(NH_4)_2SO_4$, $6H_2O$

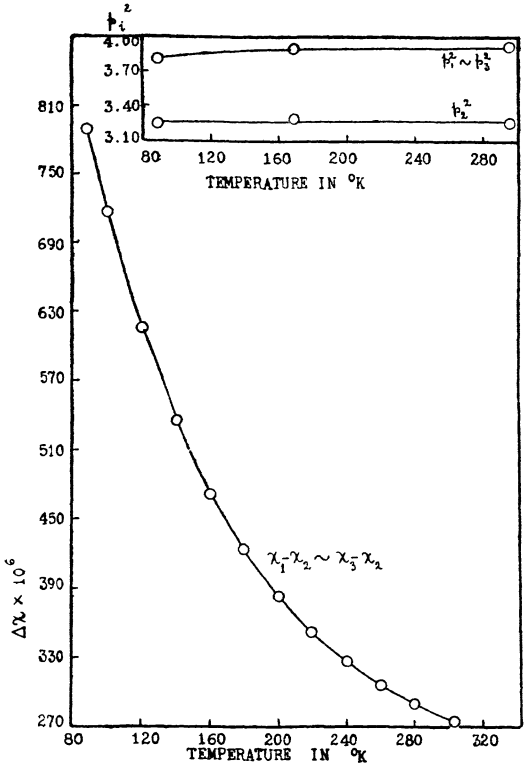


FIG. 1

Temperature Variation of Principal Anisotropies and Effective Moments of $CuSO_4$, $5H_2O$.

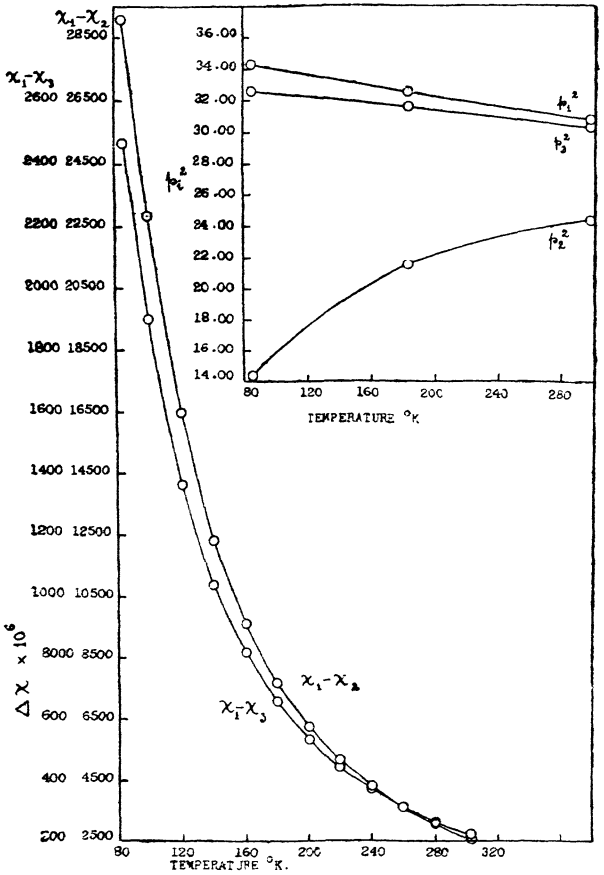


FIG. 4

Temperature Variation of Principal Anisotropies and Effective Moments of $FeSO_4(NH_4)_2SO_4.6H_2O$.

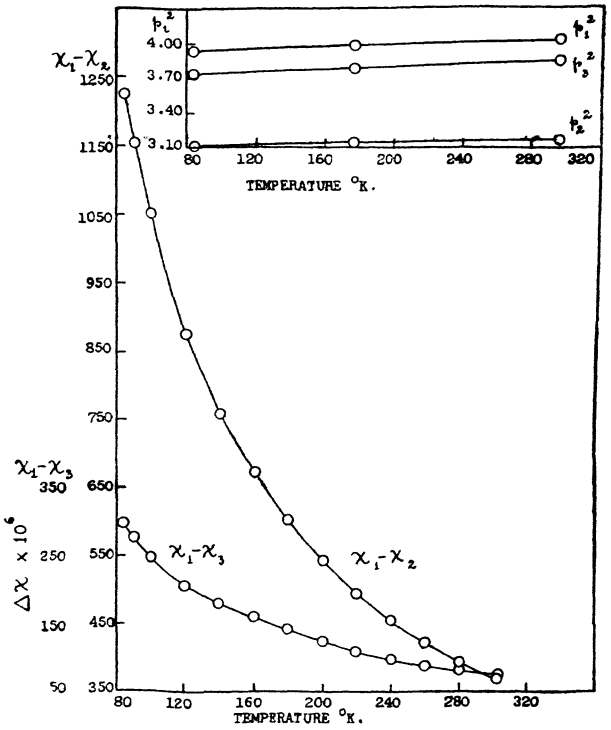


FIG. 3

Temperature Variation of Principal Anisotropies and Effective Momen of $CuSO_4\,K_2SO_4.6H_2O$

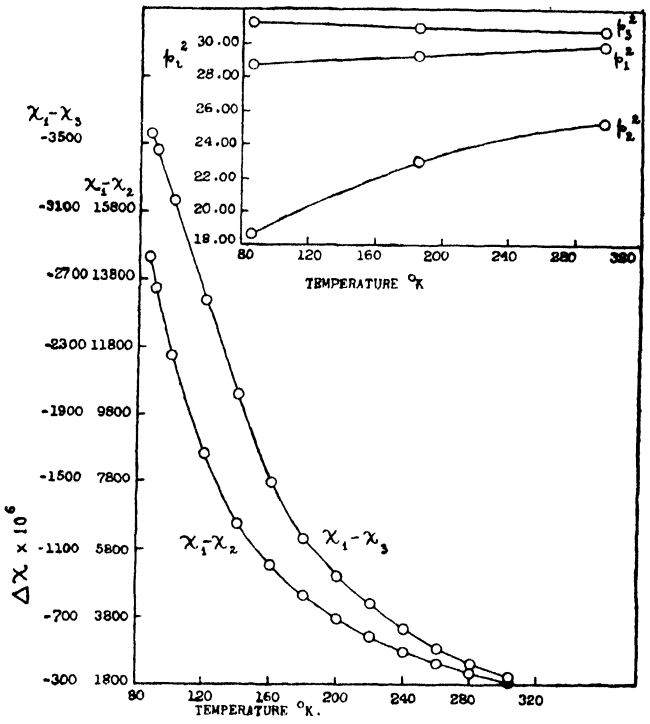


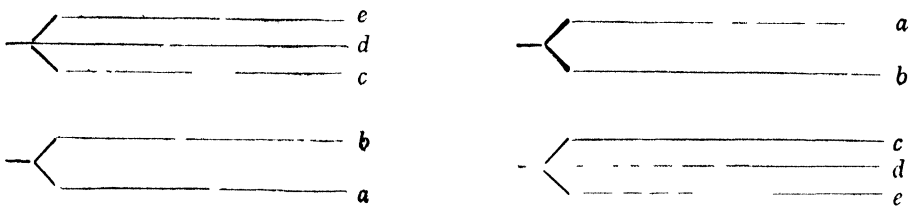
FIG. 5

Temperature Variation of Principal Anisotropies and Effective Moments of $FeSO_4.K_2SO_46, H_2O$.

DISCUSSIONS

1. *Inversion of Stark-pattern from Cu^{++} to Fe^{++} Salts*

It is known that both Cu^{++} and Fe^{++} ions are in the D-state, namely, $3d^9\ ^2D_{5/2}$ and $3d^6\ ^5D_1$ respectively. It has been shown by Bethe (1929) and Van Vleck (1932) that in a predominantly cubic field a D-state splits up into a doublet and a triplet separated to the order of 10^1 cm^{-1}. The small superimposed rhombic field separates the components of the doublet and the triplet by an amount much smaller than the above cubic separation but comparable to kT. Hence, whether the doublet is the lowest lying in the Stark-pattern or the triplet, the population of the upper components of the lowest level will be quite appreciable. Thus, the magnetic behaviour of the D-state ions will not be as simple as that of the F-state ions with singlet lying lowest. Now, the Cu^{++} ion has nine electrons in the $3d$ shell while Fe^{++} has six. Hence, their Stark-patterns in a *given* cubic field will be inverted with respect to each other (Fig. 6) and the difference in the magnetic behaviour of the two ions will depend on whether the doublet or the triplet is the lowest in one or the other. Actually, for a cubic field with positive value of the coefficient D in the expression $V=Ax^2+By^2-(A+B)z^2+D(x^4+y^4+z^4)$, the disposition of the patterns will be as given below.

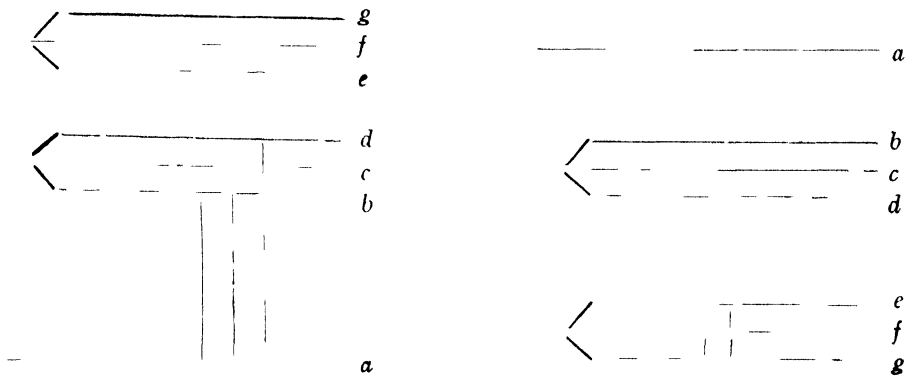


Stark-pattern for Cu^{++} in a cubic field with +ve D

Stark-pattern for Fe^{++} in the same field.

FIG. 6

In the case of Co^{++} and Ni^{++} salts we found (Bose, 1948) that such an inversion in the Stark-pattern is responsible for the striking contrast in the magnetic behaviours of the two salts and arises in the following manner (Van Vleck, *loc. cit.*) as can be readily seen from their respective Stark-patterns. (Fig. 7).



Stark pattern for Ni^{++} in a cubic field with +ve D

Stark-pattern for Co^{++} in the same field

FIG. 7

In the case of Ni^{++} in which the ground level is a singlet, the contributions from the orbital moments to the susceptibility will depend inversely on the frequencies ν, corresponding to the energy separations $a \rightarrow b$, $a \rightarrow c$ and $a \rightarrow d$, for the different directions of the incident magnetic field in the crystal. In the first place, these frequencies will be large, since they correspond to separations produced by the predominant cubic part of the field. Secondly, they will differ from one another by small amounts, since $\Delta\nu/\nu$ will be of the same order as the ratio of the separations produced by the rhombic part of the field to that produced by the cubic part. The results will be that for Ni^{++} salts (1) the contribution from orbital moments to the total effective moment cannot be large ; (2) these contributions will be practically the same along the different crystal directions, thus producing very little anisotropy. On the other hand, when as in Co^{++} the pattern is inverted making triplet level the lowest, the orbital contributions along different directions will be mainly given by the frequencies corresponding to the energy separations $g \rightarrow f$ and

$g \rightarrow e$ respectively, due to the rhombic field, which are much smaller than those due to the cubic field. Further, the separations $g \rightarrow f$ and $f \rightarrow e$ will be of comparable magnitudes. Hence we conclude (1) that the contributions from the orbital moments will be large ; (2) that the differences between these contributions along different directions in the crystal, will be comparable to their absolute magnitudes, leading to a very high anisotropy of the order of 25 to 30 % for Co^{++} in comparison with 3 to 4 % only for Ni^{++} salts, all at room temperatures, as is quite well known (Bose, 1948).

On the other hand, Tables I and II show that there is no such marked contrast between the cupric salts and the ferrous salts, in spite of the inversion of the Stark-patterns for the two. In both of them the orbital contributions are found to be large, as is shown by a comparison of the *observed* p^2 values of Cu^{++} and Fe^{++} ions, with the *spin only* values for the two ions, namely 3 and 24 respectively. Both the salts show large anisotropies of the same magnitude, $\Delta p^2/p^2 = 19$ to 24 % for the different salts at room temperatures.

One would, therefore, be tempted to attribute the negative results of the inversion to the fact that, whether the Stark-pattern is erect or inverted the ground level is a multiplet and hence would correspond to large contributions to orbital moments and to a large anisotropy. But such a simple explanation is vitiated by the interesting fact pointed out by Bethe, (*loc. cit.*) that the doublet is 'non-magnetic' *i. e.*, there can be no orbital contributions involving the frequencies corresponding to the separation of the components of the doublet ; so that the large orbital contributions in Cu^{++} salts cannot arise from the low frequency terms, as it presumably does in Fe^{++} where the ground level is a triplet. So one has to invoke, to explain the orbital contribution in Cu^{++}, the terms depending on the separation between the doublet and the triplet ; and in order to explain the large anisotropy we have further to postulate that it is only the lower of the two levels of the doublet that will be occupied, even at the highest temperature in our measurements ; in other words, to postulate a separation between the two levels of the doublet, much greater than kT even at these temperatures. The latter postulate is plausible, since, the separation produced by the rhombic part of the field, though smaller than that produced by the cubic part, can still be much greater than kT.

Thus, we should expect the orbital contribution in Cu^{++} to be much smaller than in Fe^{++}. But since, the contribution from the spin moments in Cu^{++} is also much smaller than in Fe^{++}, namely in the ratio of 3 : 24, the ratio of the orbital contribution to the spin contribution is of the same order in both the salts as actually observed. In the ferrous salts, the high anisotropy is due to the orbital contribution being different along different crystal directions—actually adding to the spin contribution along two of the directions, and acting against it along the third. The p^2 value along this direction will, hence, be less than even the *spin only* value of 24. On the other hand, in

cupric salts the high anisotropy is due to the orbital moment being confined to a single direction.

2. *Magnetic Properties of Cupric Salts*

Among the cupric salts studied by us copper sulphate penta-hydrate is the most interesting. The crystal is triclinic and from the X-ray analysis of this crystal made by Beevers and Lipson (1934), we know that it contains two molecules of $CuSO_4, 5H_2O$ in the unit cell. Further, each Cu^{++} ion is surrounded by six oxygen atoms, four of which belong to four water molecules and form a square with the Cu^{++} ion in the centre and each at a distance of 2.0 Å, and the other two oxygen atoms belong to SO_4^{--} ions located centrally above and below the square, each at a distance of 2.4 Å from the Cu^{++} ion. This octahedral arrangement of the oxygen atoms is thus not quite regular but has a tetragonal symmetry, which may be regarded as obtained from a regular arrangement by pulling out the diagonal joining the last two oxygen atoms. Presumably thus, the crystalline field in the neighbourhood of the Cu^{++} ion should also be predominantly cubic in symmetry, with a tetragonal component superposed upon it, the principal axes of the two fields being the same.

As have been shown by Krishnan and Mukherji (1936, 1938), the tetragonal axis of the field, associated individually with the two Cu^{++} ions in the unit cell of the crystal, are nearly perpendicular to each other. Further, denoting the direction of the tetragonal axis of the ion by z and the principal susceptibilities of either ion along this axis and in the plane perpendicular to it by $K_\parallel$ and $K_\perp$ respectively, and distinguishing the axes of the two ions in the unit cell by subscripts 1 and 2 respectively, they conclude that (1) $K_\parallel > K_\perp$, (2) the direction in $CuSO_4, 5H_2O$ crystal perpendicular to the z_1z_2 plane, should be one of the principal magnetic axes of the crystal, (3) the exterior and the interior bisectors of the angle between z_1 and z_2 directions should be the other two principal axes, (4) since z_1 and z_2 are nearly at right angles, the susceptibilities along the latter two axes must be nearly equal and of the magnitude $(K_\parallel + K_\perp)/2$, and that along the first axis at right angles to z_1z_2 plane equal to $K_\perp$. Denoting the two nearly equal susceptibilities by χ_1 and χ_3 respectively and the third by χ_2

$$\left.\begin{array}{ll} \text{we have} & \chi_1(\sim\chi_3) = (K_\parallel + K_\perp)/2 \\ & \chi_2 = K_\perp, \\ \text{and since} & K_\parallel > K_\perp, \\ & \chi_1(\sim\chi_3) > \chi_2. \end{array}\right\} \quad \ldots (2)$$

All these various results have been verified by Krishnan and Mukherji. Further, using the data for susceptibility at low temperatures of powdered crystal by de Haas and Gorter and from their own measurement of the anisotropy down to liquid air temperature, they conclude that though the squares of principal magnetic moments $p_1^2(\sim p_3^2)$ and p_2^2 are very different, they are both nearly independent of temperature. In other

words, all the susceptibilities follow the Curie law but with different Curie constants *i.e.* a law of the type

$$\chi_i = \frac{C_i}{T}, \quad i = 2, 3(\sim 1) \qquad \ldots (3)$$

$$C_2 = 0.399 \text{ and } C_1(\sim 3) = 0.486 ;$$

unlike the usual type of variation

$$\chi_i = \frac{C}{T - \theta_i}, \quad i = 1, 2, 3, \qquad \ldots (4)$$

where C is the same but θ's different in different directions.

We have directly measured the absolute susceptibilities at different temperatures down to 80°K along one of the directions in the crystal, namely, the one that sets parallel to the field when the crystal is suspended with 'c' axis vertical, and using the anisotropy data of Krishnan and Mukherji, calculated the values of $p_1^2 (\sim p_3^2)$ and p_2^2 for the crystal at these temperatures. The data are given in table II and are in agreement with those of Krishnan and Mukherji. The p^2 values also agree with various other authors and are given in Table III, together with p^2 values by the same authors for the two Tutton salts of copper to be discussed later.

TABLE III

p^2 For Various Copper Salts By Different Observers.

Author	$CuSO_4, 5H_2O$		$CuSO_4,(NH_4)_2SO_4,6H_2O$		$CuSO_4,K_2SO_4,6H_2O$	
	Temp.°K	p^2	Temp.°K	p^2	Temp.°K	p^2
da Haas and Görter (Leid. Comm., 210d	290.0	3.705	—	—	—	—
	169.4	3.663	—	—	—	—
	77.47	3.026	—		—	—
	14.29	3.505	—	—	—	—
Janes (1935)	—	—	295.7	3.741	296.8	3.729
	—	—	229.8	3.708	205.6	3.696
	—	—	83.3	3.660	82.1	3.657
Reekie (1939)	292.2	3.654	292.7	3.720	287.5	3.684
	80.4	3.632	79.9	3.690	78.6	3.633
	14.78	3.528	14.00	3.648	14.13	3.600
	1.58	2.634	1.60	3.642	1.60	3.579
Present Author	295.2	3.701	295.9	3.761	295.9	3.683
	168.8	3.701	225.0	3.748	176.9	3.630
	88.7	3.626	92.9	3.706	83.9	3.592

We may draw attention here to the interesting result that for the crystal of $CuSO_4, 5H_2O$, p_2^2 conforms roughly to the *spin only* value of 3, whereas the other susceptibility is considerably in excess of it, which shows, in view of the relations (2) between the principal susceptibilities of the *crystal* and the *ion* stated earlier in this section, that the contribution of the orbital moment

is practically confined to one direction, namely, to the tetragonal axis of the crystalline field in the neighbourhood of the ion. Denoting the effective moments of the *ion* by $P_{\parallel}$ $P_{\perp}$, as against the effective moments $p_1(\sim p_3)$ and p_2 of the *crystal*, we have

$$p_1^2(\sim p_3^2) = (P_{\parallel}^2 + P_{\perp}^2)/2$$
and $$p_2^2 = P_{\perp}^2 \quad \ldots (5)$$

from which we obtain :—

TABLE IV

$CuSO_4, 5H_2O$

T°K	295.2	88.7
$P_{\parallel}^2$	4.588	4.377
$P_{\perp}^2$	3.258	3.251

—from which one can see, that the contribution from the orbital moment is considerable and is confined to the direction of the tetragonal axis of the crystalline electric field. The temperature variation of the moment if any, should be also more prominent in this direction as it actually is.

The above results are interesting, since, from the 'non-magnetic' nature of the ground level which is the doublet level, we were already led to the conclusion that the orbital contribution is confined to one direction in the crystal. That when the crystalline field has tetragonal symmetry this direction should be along the tetragonal axis, is indeed to be expected, and can also be explained from direct considerations of the symmetry of the field ; since the orbital moments will be quenched almost completely along directions perpendicular to the tetragonal axis, and if any part of it is conserved it must be along this axial direction only.

In view of the fact that the magnetic anisotropies in the two cupric Tutton salts are nearly the same as in copper sulphate, it is tempting to try whether a similar cubic field with a feeble tetragonal component will also fit the observed data for these two salts. The Tutton salts as already mentioned are monoclinic and contain two Cu^{++} ions in the unit cell. Assuming the field to be tetragonal, the χ_1-axis of the crystal should be evidently the projection of the tetragonal axis of the ion on the (010) plane of the crystal. Denoting the inclination of this tetragonal axis of the ion to the (010) plane by ϕ, we get the following simple relations between the principal magnetic moments of the *crystal* and those of the *ions* .—

$$p_1^2 = P_{\parallel}^2 \cos^2\phi + P_{\perp}^2 \sin^2\phi$$
$$p_2^2 = P_{\perp}^2 \quad \ldots (6)$$
$$p_3^2 = P_{\parallel}^2 \sin^2\phi + P_{\perp}^2 \cos^2\phi$$

If the above assumptions, regarding the tetragonal symmetry of the crystal field associated with each Cu^{++} ion, be correct then we should expect $p_2^2 = P^2_{\perp}$, to have practically the *spin only* value of 3. This is actually so as will be seen from below.

TABLE V

Crystal $CuSO_4$, A_2SO_4, $6H_2O$

	Temp K	$P^2_\perp = p_2^2$	$P_\parallel^2 = p_1^2 + p_3^2 - p_2^2$
$A = NH_4$	295·9	3·330	4·622
	91·9	3·327	4·464
$A = K$	295·9	3·149	1·752
	83·9	3·107	1·562

Knowing $P_\perp^2$ we can indeed go further and calculated $P_\parallel^2$ from the observed values of p_1^2 and p_3^2 using the relation (6), since then $P^2 = P_\perp^2 = p_1^2 + p_3^2$. The values of $P_\parallel^2$ so obtained are given in the table above.

These values agree well with the values deduced from the crystal $CuSO_4$, $5H_2O$ and show (1) that the fields in the Tutton salts do have tetragonal symmetry, in spite of the fact, that in the Tutton salts, the Cu^{++} ion is surrounded by six identical oxygens all belonging respectively, to six water molecules, unlike in copper sulphate in which two oxygen atoms are different from the rest and belong to two SO_4^{--} groups; (2) that even the magnitudes of the cubic and the tetragonal parts of the field are the same in the Tutton salts as in copper sulphate. The above conclusions lend strong support to the view expressed by us in our earlier papers (Bose, 1947, 1948), and which has generally been adopted in our discussions, that in addition to the cubic part, the feeble noncubic part of the field also may be due to the immediately neighbouring atoms, and as long as these neighbours are the same and arranged in the same configuration in different crystals, the crystal fields in them also will be the same. These results, have important significance in view of the interesting theorem of Jahn and Teller (1937, 1938), that the asymmetry and the magnitude of the crystalline field are determined ultimately by the degeneracy of the ground state of the paramagnetic ion.

The six oxygens surrounding the Cu^{++} ion will be strongly bound to the ion and the group as a whole will form a more or less rigid system having tetragonal symmetry. But the binding between two such groups present in the unit cell will be much feebler and hence the two tetragonal axes may slightly change their relative orientations with change of temperature; consistent of course with the requirement of the monoclinic symmetry of the crystal of these Tutton salts, namely, that one of the groups should be the mirror image of the other. In other words, though the crystal fields and therefore, $P_\parallel$ and $P_\perp$ will be practically independent of the temperature, the angle ϕ, which the tetragonal axis makes with the (010) plane, as also its projection on the (010) plane, may change slightly with the temperature. The projection of the tetragonal axis is evidently the χ_1 axis of the crystal, and thus we can readily see how without any change in the crystalline field, either in its magnitude or in its asymmetry, there can be appreciable change in the

direction of the χ_1 and χ_2 axes of the crystal. The angle ϕ may be calculated from the relation,

$$\frac{p_1^2 - p_3^2}{P_{\parallel}^2 - P_{\perp}^2} = \cos 2\phi \qquad \ldots (7)$$

and its temperature variation for the two Tutton salts may be seen from the Table VI. We specially emphasise this point, since an explanation of the change of axis in terms of the change in crystalline field, as has been attempted by Jordahl (1934), is not only complicated but requires a large rotation of the rhombic field axes with reference to the axes of the cubic field.

TABLE VI

For the angle ϕ

Crystal : $CuSO_4$, A_2SO_4, $6H_2O$

	Temperature °K	Angle ϕ in degrees
$A = NH_4$	295.9	40 8
	91 9	31.3
A - K	295 0	41 8
	83 0	41 0

Before concluding this section we should refer to some important results obtained by Reekie (1939, vide Table III) on the mean susceptibilities of these three cupric salts at liquid hydrogen and helium temperatures. For all the three salts the effective magnetic moment, corresponding to the mean susceptibility, is practically independent of temperature down to about 14°K (as we have also found for each of the three principal moments separately and over a shorter range of temperature). But below this temperature there is a striking contrast in the behaviour of the copper sulphate on one side and the two cupric Tutton salts on the other. Whereas, in copper sulphate the value of p, comes down rapidly at liquid helium temperatures and the trend of the p^2 against T curve suggests that it may reach very low values in the neighbourhood of absolute zero; in the Tutton salts the fall in p, is very slight and its rate is of the same order as at higher temperatures. Presumably, associated with this is the observation of Ashmead (1939) that the specific heat versus temperature curve of copper sulphate shows a large hump in the region of 4°K, which is completely absent in the corresponding curves of the two cupric Tutton salts. These results do not appear to be explicable on the crystalline field theory, and indeed, at present, on any theory.

3. *Ferrous Salts Versus Cobalt Salts*

As we mentioned in an earlier section, the triplet level in the Stark-pattern of the D-levels of Fe^{++} being lowermost, there should be a large contribution from the orbital moments, and the contributions should be different

along different directions, actually adding to the spin contribution along p_1 and p_3 directions and acting against the spin along p_2 direction. Hence the large anisotropy in the crystals. We further see from the experimental data given in Table II that p_1 and p_3 have nearly the same values which vary little with temperature and they are not much different in the two salts. In cobalt salts (Bose, 1948) all the three p's tend to become temperature-independent at high temperatures, the values being very different from the *spin only* value of $p^2=15$. The experimental values for Fe^{++} show that p_1 certainly, and probably also p_3 will reach temperature-independent values at high temperatures, and it is not unlikely that those temperature-independent values may all be the same, namely, the *spin only* value corresponding to $p^2=24$. If this is so it would mean that high frequency contributions in Fe^{++} are much less than in Co^{++}.

ACKNOWLEDGMENT

The author takes this opportunity of thanking Prof. K. S. Krishnan, D.Sc., F.R.S., for his kind interest and help in the series of investigations on the iron group of salts, of which the present paper is the last, which were completed before 1941 but could not be published so long due to unavoidable circumstances.

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